



Enhancement in the Photoluminescence Properties of $\text{SiO}_2\text{:Ge}$ Embedded in a Polymeric Matrix

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ABSTRACT

Polymer films of styrene butadiene copolymer (SBC) mixed with $\text{SiO}_2\text{:Ge}$ powder were successfully obtained by the drop casting method. The SBC concentration (in chloroform solution) was 10%_{w/v}, and the $\text{SiO}_2\text{:Ge}$ powder was mixed (mass ratio 80:20 respectively). The thicknesses of the films obtained were 50, 100, and 200 μm . In addition, polymer films of polytetrafluoroethylene (PTFE) preparation (60% dispersion in water), were obtained mixing 2 ml of PTFE and 0.05g of $\text{SiO}_2\text{:Ge}$ powder with a mass relation of 98% polymer and 2% $\text{SiO}_2\text{:Ge}$. The photoluminescence emission spectra (PL) of SBC doped with $\text{SiO}_2\text{:Ge}$ resulted in similar characteristics to those for $\text{SiO}_2\text{:Ge}$ powders, although their intensity shows an increase 3.5 times approximately, compared with the pure powder. On the other hand, the PTFE films with $\text{SiO}_2\text{:Ge}$ present just one peak in the PL emission at 439 nm but their intensity increases 18 times respect to the powder. The photoluminescence excitation (PLE) spectra of the $\text{SiO}_2\text{:Ge}$ powders show the characteristic peaks at 248 nm (most intense) and at 366 nm. However, when the powder is embedded either in SBC or PTFE the peak at 366 nm shows an important increase which seems to indicate an energy transfer from the polymer to the $\text{SiO}_2\text{:Ge}$.

1. Introduction

In the last decade the research in films of SiO_2 doped with germanium has increased, due to their potential applications in optoelectronics and solar cells [1,2]. However, it is necessary to improve the photoluminescence (PL) properties to make them more attractive for these applications. For that reason, some research groups have implemented strategies as thermal treatments [3], the confinement of Ge in a sandwiched structure [4] or use a polymer as a matrix to improve their PL properties. In this work, $\text{SiO}_2\text{:Ge}$ powders were embedded in two different polymers, the first was styrene butadiene copolymer (SBC) whose transmittance characteristics are very interesting for optoelectronic applications, obtaining an improvement in the PL intensity. On the other hand, the polymer films with PTFE shows an enhancement in the PL intensity of around 18 times.

2. Experimental Overview

2.1 Materials

$\text{SiO}_2\text{:Ge}$ commercial optical fiber manufactured by Nokia Cable, with 150 μm diameter was used. Ge concentration in the fiber was determined by EDS, resulting 0.3 %. Styrene butadiene copolymer (SBC) was provided by Ineos Styrolution Co. identified as Styrolux 3G46, and polytetrafluoroethylene preparation (60 wt% dispersion in H_2O) (PTFE dispersion) was purchased from Sigma Aldrich.

2.2 Preparation of $\text{SiO}_2\text{:Ge}$ Powders

The optical fiber was cut in stretches of 30 cm and the plastic material that protects it was removed. Then the fiber was cleaned with ethanol. Finally, the optical fiber was cut in little pieces and pulverized until obtaining uniform powders.

2.3 Polymer - $\text{SiO}_2\text{:Ge}$ Films

2.3.1 SBC - $\text{SiO}_2\text{:Ge}$ films

The polymer films were prepared by the drop casting method using $\text{SiO}_2\text{:Ge}$ powders. The powders were dispersed in 5 ml of chloroform with a concentration of 2%_{w/v}. The dispersion was sonicated for 1 h and then was mechanically stirred during 30 min. Then, SBC was added in the previous dispersion at a concentration of 10%_{w/v} in chloroform. From the final mix some aliquots (0.5, 1 and 2 ml) were dropped into different small beakers. The films with different thicknesses were obtained after the solvent was evaporated.

2.3.2 PTFE dispersion - $\text{SiO}_2\text{:Ge}$ films

The polymer composites were obtained by a rot molding process, using PTFE dispersion and $\text{SiO}_2\text{:Ge}$ powders. First, 3 ml of PTFE dispersion (whose density is 1.5 g/ml at 25°C) was added in a 10 ml beaker, then 40%_{w/v} of $\text{SiO}_2\text{:Ge}$ powders were added and were mechanically stirred during 30 min. Then this solution was heated at 90°C until water has evaporated. Finally, the material obtained was processed by a rot molding process until obtaining three different thickness polymer films.

2.4 Characterization

$\text{SiO}_2\text{:Ge}$ and the polymer films were characterized by Fourier transform infrared spectroscopy (FTIR) using a Nicolet 6700 FTIR spectrophotometer in the 400 - 4000 cm^{-1} range. In the case of $\text{SiO}_2\text{:Ge}$ powders, they were embedded in KBr pellets to perform the FTIR measurements. The mass spectroscopy was obtained with a Discovery TGA 5500 with a Discovery mass spec of TA Instruments. Photoluminescence emission (PL) and excitation (PLE) spectra were measured at room temperature with an Edinburgh Instruments fluorescence equipment, Mod. FLS980.

3. Results and Discussion

3.1 FTIR Analysis

Figure 1 shows the FTIR transmission spectra for a) $\text{SiO}_2\text{:Ge}$ powders, b) $\text{SiO}_2\text{:Ge}$ embedded in SBC, and c) pure SBC. The IR spectrum of $\text{SiO}_2\text{:Ge}$ powders (Figure 1a) exhibits the stoichiometric vibrations from SiO_2 at 450 cm^{-1} , 800 cm^{-1} , and 1080 cm^{-1} , which correspond to Si - O - O rocking, bending and stretching, respectively [4, 2]. Additionally, a shoulder at 1020 cm^{-1} is shown, that is related to nonstoichiometric SiO_x ($x < 2$) [4]. However, the vibrations attributed to Ge - O - Ge (580 - 870 cm^{-1}) [5] are not present. In the case of Figure 1c, the characteristic

vibrations of SBC at 543 cm^{-1} , 701 cm^{-1} , 755 cm^{-1} , and 1451 cm^{-1} are observed, corresponding to C - C, C - H, out of plane bend, the ring mode of styrene and scissors mode of CH_2 vibration modes, respectively [6]. Finally, the polymer films doped with $\text{SiO}_2\text{:Ge}$ show an important contribution from SBC. These spectra show all the characteristic vibrations from SBC and only one vibration of $\text{SiO}_2\text{:Ge}$ that is observed at 460 cm^{-1} and corresponds to a Si - O - Si rocking mode.

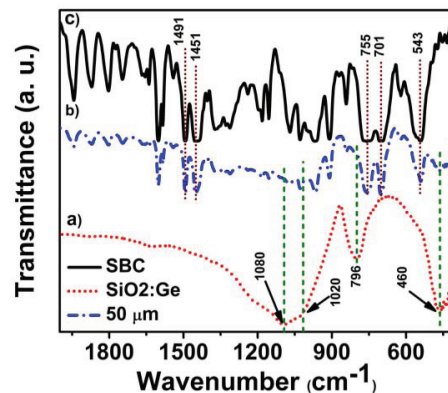


Figure 1. FTIR transmission spectra for a) $\text{SiO}_2\text{:Ge}$ powders, b) $\text{SiO}_2\text{:Ge}$ embedded in SBC and c) pure SBC.

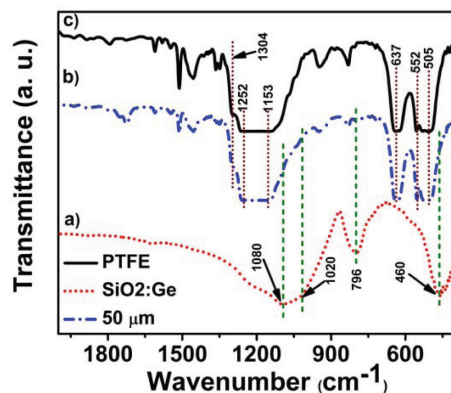


Figure 2. FTIR spectra for a) $\text{SiO}_2\text{:Ge}$, b) $\text{SiO}_2\text{:Ge}$ embedded in PTFE and c) PTFE.

Figure 2 exhibits the FTIR spectra for a) $\text{SiO}_2\text{:Ge}$, b) $\text{SiO}_2\text{:Ge}$ embedded in PTFE and c) PTFE. Figure 2c, shows the characteristic vibrations of PTFE that are located at 505 cm^{-1} , 552 cm^{-1} , 637 cm^{-1} , 1153 cm^{-1} , 1252 cm^{-1} and 1304 cm^{-1} that correspond to F - C - F bending, rocking, wagging, very strong asymmetric stretching, shoulder asymmetric stretching and stretching of C - C, respectively [1,2,7,8]. In the case of $\text{SiO}_2\text{:Ge}$ embedded in PTFE (Figure 2b) is observed the characteristic vibration from PTFE, however neither vibration from $\text{SiO}_2\text{:Ge}$ powders was observed, maybe due to the $\text{SiO}_2\text{:Ge}$ powders are completely embedded. If

these materials are embedded completely, the PL spectra could be changed compared with the pure powders.

3.2 Thermal behavior

Thermal behavior of SBC, PTFE and $\text{SiO}_2\text{:Ge}$ powders embedded in these polymers were studied by TG-MS in the temperature range 20 - 640°C. In Figure 3 the thermograms are shown, with a heating rate of 10°C/min under Helium environment. In Figure 3 the curves 1 and 2 show that the SBC and $\text{SiO}_2\text{:Ge}$ powders embedded in this polymer have similar thermal behavior. These materials present a fast loss weight at ~370 °C and the complete degradation around 500°C. Also, the main decomposition comes from the SBC monomer (C_8H_8) (curve a in Figure 3) and is bigger in the polymer composites (curve b in Figure 3). The last one may be due to $\text{SiO}_2\text{:Ge}$ powders, which are very stable at high temperatures because this material is uniformly embedded, which improves their thermal resistance.

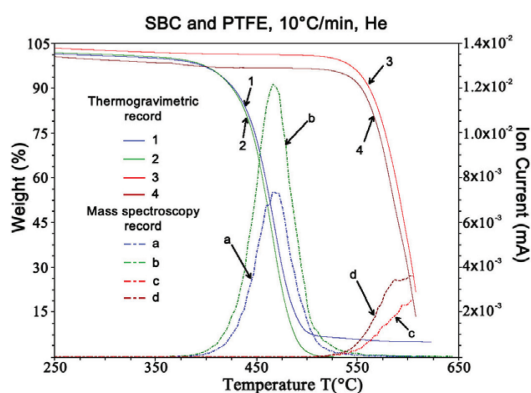


Figure 3. Thermograms and mass spectroscopy records of SBC (curves 1 and a), composites of SBC (curves 2 and b), PTFE (curves 3 and c) and composites of PTFE (curves 4 and d).

In the case of PTFE and the composites of PTFE with $\text{SiO}_2\text{:Ge}$ powders, the thermal stability observed is observed until ~550°C. In this case, the monomer decomposition (C_4F_4) on the PTFE composites (curve d in Figure 3) is bigger than PTFE polymer films (curve c in Figure 3), maybe, because of the concentration of $\text{SiO}_2\text{:Ge}$ powders is lower. For this reason, it is believed that if the concentration of $\text{SiO}_2\text{:Ge}$ powders in PTFE solution increases, the decomposition of the monomer will be reduced.

3.3 UV-vis transmittance of composites

Figure 4 shows the transmittance in the UV region of the SBC composites obtained by the drop casting method. Clearly, the optical transmission decreases as the thickness

increases. The optical transmission corresponding to the PTFE is too small to be measured.

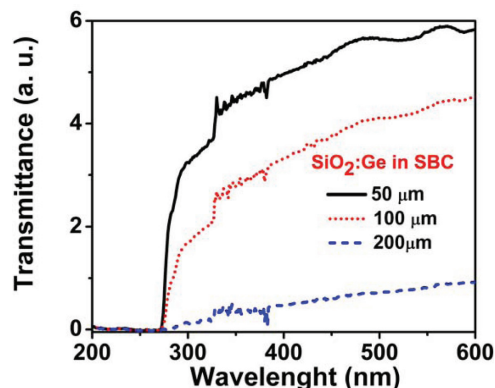


Figure 4. Transmittance of SBC films doped with $\text{SiO}_2\text{:Ge}$ at different thicknesses.

3.4 Photoluminescence Properties

3.4.1 SBC doped with $\text{SiO}_2\text{:Ge}$ powders

The photoluminescence emission (PL) and excitation (PLE) spectra of $\text{SiO}_2\text{:Ge}$ powder, SBC, and the composites of different thicknesses are shown in Figures 5a and 5b. In Figure 5a the samples of pure $\text{SiO}_2\text{:Ge}$ powders have an emission band in the blue region (400 – 500 nm) where two peaks at 417 and 440 and a shoulder at 469 nm are observed. The peak at 417 nm corresponds to transition $T_x(T\pi) \rightarrow S_0$, which is attributed to the GeO color centers in $\text{SiO}_2\text{:Ge}$ [4,5]. In the case of the band at 469 nm it can be associated to a radiative recombination between electrons and holes in GeO_2 that may be present in the $\text{SiO}_2\text{:Ge}$ powder [9]. However, the reported peak is very broad (400 – 600 nm). For that reason, it is believed that the peak at 440 nm is part of that recombination.

The enhancement in the PL spectra was 3.5 times, approximately, in the composites with 50 μm compared with those of the pure powders. Also, the peaks of the spectra are narrower, the peak at 440 is higher and the slight shoulder at 469 is more noticeable. This improvement is due to an energy transfer from SBC polymer to the $\text{SiO}_2\text{:Ge}$ that facilitates the transition of $T_x(T\pi) \rightarrow S_0$ associated with the absorption at 329 nm of GeO . The enhancement in this transition is important because it is not frequently observed. The common transition in $\text{SiO}_2\text{:Ge}$ is $S_1 \rightarrow S_0$ associated with the absorption of GeO at 242 nm, which is appreciated in the pure powders [10], and the PL reduced as the thickness increases, due to the transmittance reduction that does not allow a good recombination [11].

The PLE spectra of $\text{SiO}_2\text{:Ge}$ powders show their main peak at 248 nm which is attributed to $S_1 \rightarrow S_0$ transition of

the GeO color centers [12,4], however, an efficient energy transfer from the SBC polymer to the powders exhibited an increase in the peak associated with $T_{\Sigma}(T\pi) \rightarrow S_0$ transition, present at 365 nm that decreases as the thickness increases. Also, as the thickness increases, a band at 317 nm is observed, maybe as a contribution of the polymer [13]. The origin of the decrease of the PL spectra as the thickness increases is in accordance with the transmittance spectra shown in Figure 4.

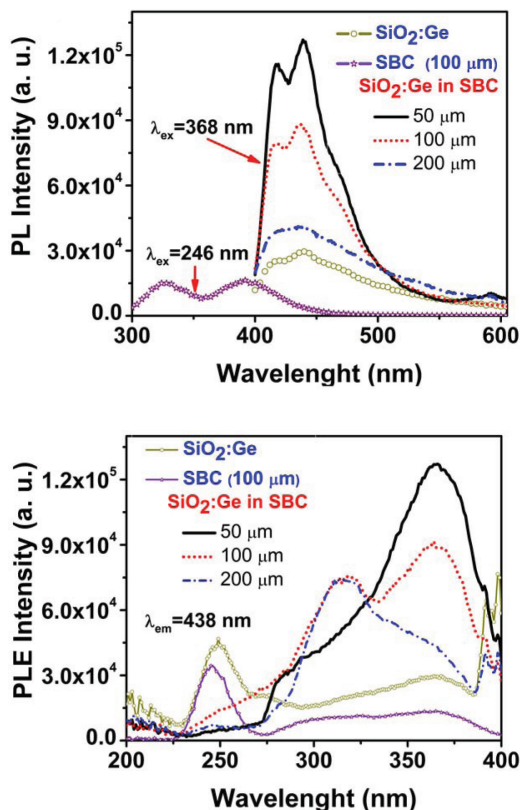


Figure 5. Photoluminescence and photoluminescence excitation spectra of the samples indicated. For PL spectra the excitation wavelength was 246 nm for the pure SBC polymer, the other samples were excited with 368 nm. For PLE the detection energy corresponds to $\lambda_{em} = 438$ nm in all cases.

3.4.1 PTFE doped with $SiO_2:Ge$ powders

PL and PLE of $SiO_2:Ge$ powders, PTFE and composites of PTFE are exhibited in Figures 6a and 6b. PL spectra of the PTFE composites at different thickness exhibits a similar behavior, however, it is different from the spectra of $SiO_2:Ge$ pure powders. In this case is observed a broadband from 400 to 550 nm with its main peak at 439 nm, with an enhancement in its intensity of around 20 times. As mentioned before, this polymer films have a poor transmittance. PLE spectra of PTFE exhibit two peaks

and a shoulder at 249, 288 and 341 nm. This PL intensity is bigger than $SiO_2:Ge$ powders and can be overlap all its spectrum. PTFE composite films shows similar behavior as SBC composites, however, it is observed an additional peak at 288 nm attributed to a PTFE emission. The main peak at 341 nm is attributed to $T_{\Sigma}(T\pi) \rightarrow S_0$ transition from GeO color centers. In this case the enhancement in the intensity is due to an efficient energy transfer from the PTFE polymer to the $SiO_2:Ge$ powders due to a better overlapping. It is important to note that this intensity increases as the thickness increases, however, when the thickness was around 1mm its PL intensity did not exhibited a big change between this thickness and 200 μm, due to the poor optical transmittance of the polymer [14].

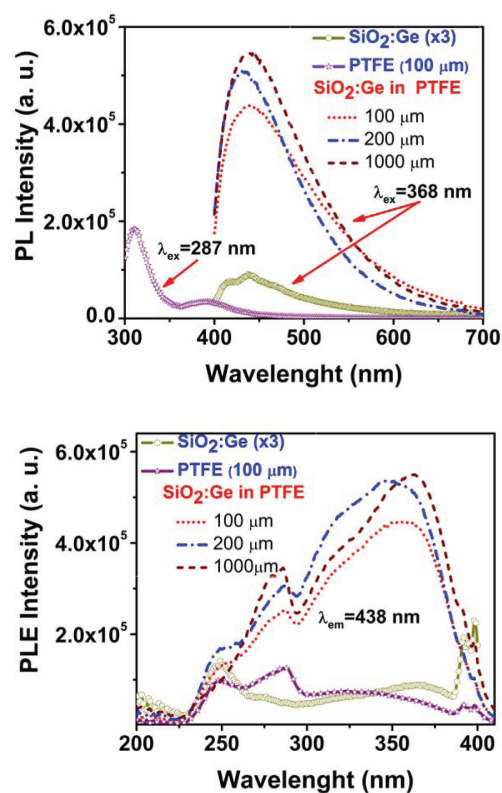


Figure 6. Photoluminescence and photoluminescence excitation spectra of the samples indicated. For PL spectra the excitation wavelength was 287 nm for the pure PTFE polymer. The other samples were excited with 368 nm. For PLE the detection energy corresponds to $\lambda_{em} = 438$ nm.

4. Conclusions

Thin films of $SiO_2:Ge$ powders embedded in two polymeric matrices were successively obtained. The polymers are (a) styrene butadiene copolymer (SBC) and (b) polytetrafluoroethylene

(PTFE). The obtained films have thermal stability up to 370°C for the first one and up to 550°C for the other, respectively. The photoluminescence properties of both polymeric structures were enhanced by an efficient energy transfer between the SBC and PTFE polymers to SiO₂:Ge powders. This is validated by the overlap of the PL excitation spectra of SiO₂:Ge powders with the polymer PL emission spectra. The PL spectra are associated with the color centers of germanium that are present as it can be observed in the FTIR spectra by the vibrations at 460, 796, 1020, and 1080 cm⁻¹.

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